



# A urea-modified polydiacetylene-based high temperature reversible thermochromic sensor: Characterisation and evaluation of properties as a function of temperature

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## ABSTRACT

Modification of polydiacetylene (PDA) with a small compound capable of forming multiple hydrogen bonds resulted in new and improved qualities such as high-temperature reversible thermochromism and higher melting temperature. Several distinct colours were exhibited to indicate different temperatures. Polydiacetylenes often suffer from irreversible thermochromic transitions and that limits their applicability in sensor development. A simple thermochromic PDA sensor that exhibits reversible thermochromism up to 150 °C is reported. This was achieved by introducing urea to the head group of 10,12-pentacosadiynoic acid (PCDA) and shining 254 nm UV light to the resulting fine powders to form a deep-blue-coloured poly-pcd-urea. Thermochromic and thermal properties of the PDA were investigated using ultraviolet–visible (UV–vis) and X-ray diffraction (XRD) spectroscopic techniques; and thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses. UV–vis studies revealed that poly-pcd-urea returned to its original blue colour when it was heated up to 150 °C. DSC and XRD revealed that the reason for loss of reversibility was probably because poly-pcd-urea melted at 151 °C and upon solidifying did not fully recover the crystalline structure responsible for its blue colour. TG analysis showed that the polymer was thermally stable up to 315 °C.

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## 1. INTRODUCTION

Temperature is essential for many natural and engineered processes necessary for everyday life, hence its measurement and monitoring is crucial. Different processes require different temperature ranges and therefore, different temperature sensing concepts or devices have been devised to suit these processes [1–3]. Many studies have shown that temperature sensing can be achieved using low cost thermochromic materials that change colour depending on the temperature of the environment. For the construction of thermochromic materials, polydiacetylenes (PDAs) are among the most investigated compounds due to their ability to exhibit a distinct chromic transition from blue to red upon being exposed to various stimuli such as organic solvents [4–6], biomolecules [7,8], metal ions [9–13], mechanical impact [14] and heat [14–28]. However, PDAs often suffer from irreversible chromic transitions,

which limit their utilisation in applications where repeated sensing or monitoring is required [29–31]. PDAs often have a long alkyl side chain that melts sometimes at moderate temperatures and causes low-temperature thermochromism that is not suitable for high temperature sensing. The most investigated diacetylene (DA) monomer, 10,12-pentacosadiynoic acid (PCDA) often suffers from this negative aspect [32]. It has been shown, however, that suitable modification of the head group can alter the thermochromic properties of polydiacetylenes [28,33–37]. Strong electrostatic interactions such as hydrogen bonding [36], and ion chelation [18,25,38], appear to be the driving factor in the preparation of reversible thermochromic sensors. For instance, by incorporating a molecule that possesses the ability to form multiple hydrogen bonds with neighbouring molecules, the inter- and intra-molecular interactions increase within the PDA structure. These increased interactions in turn increase the colour-transition temperature and the stability of the PDA against heat, and sometimes impart reversible thermochromism on the PDA [16,28,35,36,39]. Furthermore, it is important that the DA is able to polymerise and form a blue sensor by itself upon illumination with UV<sub>254</sub> light. The

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requirement for this is that the head group must be positioned in such a way that it allows for self-assembled monomers to form in order for polymerisation to be possible [15,28]. In some cases, the incorporation of long-chain alcohols or large polymeric molecules managed to shift the transition temperature but failed to impart reversible thermochromic effects to the PDA [29–31]. In view of the above, it was reasoned that a relatively small molecule capable of forming multiple hydrogen bonds can satisfy the requirements for self-assembly while the network of hydrogen bonds amongst the head groups provides thermal stability.

In a recent study by Yoon et al., a bisurea-modified PDA was synthesised and exhibited excellent thermochromic properties due to hydrogen bonding provided by the intermediate bisurea groups [40]. In this study, we use urea as a modifier to PCDA in a simple two-step reaction to prepare a reversible PDA-based thermochromic sensor. In contrast to the bisurea modification reported by Yoon et al., the current modification results in the formation of a terminal N-acylurea as the new head of the DA.

Among the small compounds that were considered as modifiers, such as ethylene glycol, ethylene diamine, urea, etc., only urea had a relatively high number of sites for possible hydrogen bonding and was, therefore, chosen for the modification of the head group of the diacetylene prior to polymerisation. According to our knowledge, only a few studies have been reported on the use of urea as a PDA modifier for use in thermochromic sensor application. The N-acylurea is expected to strengthen the head groups interaction in the PDA system by providing extensive hydrogen bonding and, therefore, enhance the system's ability to withstand heat. That should render the PDA sensor with improved thermochromic behaviour.

## 2. EXPERIMENTAL SECTION

### 2.1. Materials

10,12-pentacosadiynoic acid (PCDA, 97%, HPLC) and urea (ACS reagent, 99.0–100.5%) were purchased from Sigma-Aldrich, Germany. Dichloromethane (DCM, 99.5%, GC) was purchased from Associated Chemical Enterprise (ACE), South Africa, and was dried over magnesium sulphate (97%, anhydrous reagent grade, Sigma-Aldrich, Germany) before use. Dimethyl formamide (99.7%, reagent grade) was a product of Sigma-Aldrich, Germany. Pyridine (99.5%, GC) was bought from Associated Chemical Enterprise (ACE), South Africa.

### 2.2. Synthesis of pcd-urea

The synthetic procedure was adopted from Ji et al. [41] with modifications. 10,12-pentacosadiynoic acid (PCDA) (1.0081 g, 2.69 mmol) was dissolved in 20 mL dried DCM and filtered into a dry 100 mL round bottom flask through a 0.45  $\mu\text{m}$  PTFE syringe filter to remove prepolymerised PCDA. To this solution, oxalyl chloride (0.5 mL, 5.82 mmol) was added dropwise while stirring at room temperature. The reaction solution was allowed to stand for 2 h with occasional release of the gases from the flask until all the evolution ceased. In order to catalyse and complete the conversion of PCDA to 10,12-pentacosadiynoyl chloride (PCDCI), a drop of DMF was added to the flask and reaction was allowed for an extra 2 h. The solution was concentrated by removing DCM under reduced pressure, after which the product was collected as a yellow-brown liquid. Urea (0.1501 g, 2.50 mmol) was ground into a fine powder and dispersed in dry DCM (20 mL) under sonication for 3 min in a round bottom flask. Pyridine (0.2 mL, 2.48 mmol) was added to the flask. While stirring the mixture at room temperature, PCDCI was slowly added and was allowed to react with urea for 24 h. The off-

white solid was separated from the liquid as a very fine powder and was washed using DCM (2  $\times$  10 mL) and then deionised water (3  $\times$  15 mL), dried at room temperature and stored for later use.

### 2.3. Preparation of poly-pcd-urea colloids and powders

To form poly-pcd-urea colloids, pcd-urea (0.01 g) was placed in a vial and 4 mL of deionised water at 75–80 °C was added. The mixture was sonicated for 30 min while maintaining the temperature and then cooled down to room temperature to form a clear dispersion. The vial was covered with aluminium foil and stored at 4 °C for 24 h. Colloids of poly-pcd-urea were formed by shining UV<sub>254</sub> light on top of the uncovered vial for 5 min. A blue colour was observed which confirmed the polymerisation of the pcd-urea monomers to form poly-pcd-urea. Poly-pcd-urea powder was formed by directly shining UV<sub>254</sub> light to a thin layer of loosely packed pcd-urea white powder for 2 min. The white powder turned to a deep blue colour confirming the formation of poly-pcd-urea powder.

### 2.4. Measurements

Fourier-Transform Infrared Spectroscopy (FTIR) samples were prepared by mixing with potassium bromide (KBr) to make pellets or analysed as they were using the attenuated total reflectance (ATR) accessory. All spectra were collected on a Perkin Elmer Spectrum 100 FT-IR Spectrometer at 16 scans, 4  $\text{cm}^{-1}$ . <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were collected with a Bruker 500 MHz Avance III HD instrument (Germany). PCDA was dissolved in deuterated chloroform (CDCl<sub>3</sub>) and magic angle spinning (MAS) solid-state NMR was performed for pcd-urea. A Shimadzu UV-2450 UV-vis Spectrophotometer (Shimadzu, Japan) was used for both liquid and solid samples. For liquid samples, a quartz 1 cm wide cuvette was used while for solid samples a level and uniform barium sulphate bed was prepared in an aluminium sample pan, on which a small amount of the sample was spread in the middle and levelled. The diffuse reflectance accessory of the instrument was used for collecting the spectra of the solid samples. Scanning electron microscopy (SEM) was performed using a Tescan Vega3 XMU microscope (Czech Republic). Samples were sputter coated once with a layer of carbon prior to morphological studies at 20 kV. Crystallinity was investigated with X-ray diffraction (XRD) spectroscopy on a Rigaku Ultima IV X-ray Diffractometer (Japan). The X-ray source was CoK $\alpha$  radiation. Thermal analysis was performed in the form of thermogravimetric (TG) analysis on a Perkin Elmer TGA 4000 Thermogravimetric Analyser under nitrogen (N<sub>2</sub>) atmosphere at 20 mL/min flow rate and ramping rate of 10 °C/min from 35–800 °C. Differential scanning calorimetry (DSC) was also performed under an atmosphere of N<sub>2</sub> flowing at 20 mL/min and a ramping rate of 10 °C/min from 40–250 °C. The instrument used was a Shimadzu DSC-60 differential scanning calorimeter.

## 3. RESULTS AND DISCUSSION

### 3.1. Determination of the chemical structure

After synthesis, FTIR spectroscopy was used to confirm the attachment of urea to PCDA. The synthetic route is shown in Scheme 1. The FTIR spectra of PCDA, urea and pcd-urea are presented in Fig. 1. Characteristically, PCDA has a strong broad peak that is centered at  $\sim 2915 \text{ cm}^{-1}$  that represents the hydroxyl (–OH) group of the acid. The vast CH<sub>2</sub> network of PCDA may have overlapped with the –OH group. The peak at  $1696 \text{ cm}^{-1}$  (Fig. 1a) was attributed to the C=O double bond of the acid while the two peaks at 2137 and  $2179 \text{ cm}^{-1}$  were assigned to the two acetylene groups of PCDA. The reaction between urea and PCDA occurs at the head group of PCDA by replacing the –OH group of PCDA with an amide

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